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PARTICULARITIES OF THE TECHNOLOGY OF HIGH-DENSITY TECHNICAL CERAMICS. SINTERING OF OXIDE CERAMIC

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Activated sintering of powders with different prehistory is examined. It is shown that there exist two particle-size ranges — greater or smaller than 1 μm , where the mechanisms of densification and hardening are substantially different. The general character of the deformation — diffusion-viscous flow — remains unchanged.

The term oxide ceramic is ordinarily understood to mean a single-phase inorganic material prepared by sintering power blanks consisting of mono-oxides or their compounds. Sometimes, they can also be multiphase materials, for example, eutectic compositions or compositions containing glass. Ceramic articles, with the exception of widely used goods, have a technical use, and they must meet special requirements [1].

The term sintering refers to the formation of a monolithic body from powder materials at elevated temperature [2]. It is based on the mechanisms of mass transfer in the solid phase. We note that this process is very important in a complete procedure. Indeed, there exist only two methods of mass producing inorganic solids in a monolithic form. One is casting melts in molds followed by solidification and the other is high-temperature sintering of powder blanks. As a rule, the first method is used to obtain mainly articles from metals and alloys and the second method is used to obtain ceramic articles. However, powder metallurgy where the methods of ceramic technology are used to fabricate articles from metals and alloys has advanced substantially in the last few years [3]. Casting from melts is also used to produce some type of ceramic articles [4].

The existing works on sintering processes, primarily sintering of metal powder, are summarized in the monograph by Ya. E. Geguzin [5]. The author bases his exposition on two basic physical ideas: Ya. I. Frenkel's idea [6] that surface

tension is the driving force for sintering and B. Ya. Pines's idea [7] that sintering proceeds by the viscodiffusion mechanism. It is assumed that the structure of the powder particles is crystalline. Primarily volume diffusion fluxes are taken into consideration at all stages of the process; the presence of surface mass transfer is taken into account as a particular case.

Even though the experimental data conform to the approaches presented in [5] on a conceptual level, some processes occurring during sintering of materials, especially ceramics, still remain unclear. This is probably due to the fact that the author of Ref. 5 chose a purely physical model description of the processes. Consequently, important aspects, specifically, the role of physical – chemical particularities of the structure of the powders and their surfaces dropped out of the analysis. For example, the behavior of real powders with their large variance of the particle size is difficult to describe within the framework of simple models. In addition, the author's hypothesis that points of contact between the particles remains stationary during sintering is of little use in studying the flow of highly disperse powders. The role of the structure of the particles at different stages of sintering from the standpoint of the structure of their interior volume and surface is clearly not adequately shown. Specifically, the compounds comprising ceramic powders and possessing an ion-cation type chemical bond have a complex crystal structure. This is because such crystals are made up of two or more sublattices of chemically different ions with different radii as well as the sign and magnitude of the ionic charge [8]. The large magnitude and the directionality of the bonds between the anions and cations dictate their low mobility and thereby the high stiffness and low deformability. All cooperative movements

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of the elements — boundaries, dislocations — are practically not observed. As a result, the viscosity of the ceramic is very high, even at premelting temperatures [9].

The purpose of the present work is to describe the phenomenological picture of the behavior of oxide powders during sintering taking into consideration the experimental data which have now been accumulated.

Energy (activation) must be supplied to accelerate mass transfer during sintering of a ceramic [10]. On the basis of the well-known equation $PV = RT$ this can be accomplished by increasing the temperature T , which is ordinarily termed thermal activation, while deformation is accomplished by means of diffusion via vacancies.

The high viscosity of solids also makes it possible to use other mechanisms of activation, which are associated with energy accumulation in solids by creating metastable structures, specifically, the formation of free surfaces of particles as well as the formation of defects on the surfaces of the particles and in their volume. The elevated energy of such structures is added to the driving force of sintering and is spent (dissipated) in mass transfer processes. It is shown in [10] that energy accumulation is observed during the formation of new surfaces, surface defects in the form of sites, steps, ledges, depressions, angles, and so forth as well as zero-, two-, and three-dimensional defects.

It is important to note that the accumulated energy of surfaces and the volume of particles is manifested during sintering — the body strives to dissipate it on the annihilation of structural imperfections. At the same time, other methods of activation noted in [10], specifically, heating and introducing modifying additives, only increase the rate of the process (i.e., they accelerate its kinetics) but have no effect on the driving forces (i.e., the dynamics), which predetermine the direction and course of the process.

We underscore once again that all processes involved in the sintering of a ceramic require thermal activation in order to decrease the viscosity of the body, which makes it possible to conduct these processes in a time convenient in practice. Here, surface tension is the driving forces for mass transfer during sintering.

Ordinarily, the surface tension is considered to be the work required to form a unit area of surface separating phases (bodies) at constant temperature [2]. Often, it is also defined as the force acting on unit length of the contour of a surface separating phases and striving to minimize this surface.

As a result of this force, in the absence of external effects, a drop of liquid strives to become spherical. Surface tension is taken into account in the thermodynamic energy balances, i.e., the excess potential energy of the matter at the surface of a body as compared with the energy in the bulk. It is the driving force that cause particles to coalesce (sinter) [5].

The first cause of phenomena occurring at the surface of a body is the partial compensation of the chemical bonds of external atoms. As a result, a total force directed into the interior volume of the body arises. The degree of bond compensation can be different depending on the location of a spe-

cific atom (the surface of a boundary, step, corner, or ledge). In such cases one can talk about an atom occupying different sites for different surface defects and possessing the corresponding surface energy. There can be so many such atoms that the surface loses its crystalline structure — it becomes amorphous, which is observed experimentally [11].

During the formation of a body from individual particles in sintering processes grain boundaries remain the points of contact between the particles; here, surface tension is transformed into boundary tension. The cause of this phenomenon is still the same — incomplete compensation of chemical bonds as a result of the “nonideality” of the adjustment of the boundaries of neighboring particles, since the conditions for adjustment are far from equilibrium. A similar conclusion also applies to a dislocation tube, so that often one talks about dislocation tension. Finally, the field generated by the forces of chemical bonds is also distorted around vacancies (i.e., lattice sites without an atom).

All lattice distortions and deformations examined above make their own contribution to the increase of the energy of a real solid body as compared with the energy of an ideal single crystal [12–14]. A body strives to shed this excess in dissipation processes of deformation during sintering.

We call attention to the characteristic features of the deformation processes occurring in different bodies [15]. Amorphous bodies, similarly to liquids, exhibit viscous flow, which is realized cooperatively by a group of atoms by means of shear, rotation over short distances (less than the interatomic distance), since their chemical bond exhibits spherical symmetry, all atoms are equivalent, and there no preferred directions, i.e., no orientation. All bonds are equivalent, and their adjustment over a macrovolume occurs without difficulty. When the crystal lattice is formed, a predominant direction of the bonds appears and this determines the orientation of the motion of individual elements. A metal lattice, whose elements are interchangeable, is quite simple, and cooperative displacements in definite crystallographic directions by means of shear, turning of dislocations, block and crystal boundaries, and other lattice defects of over short distances (less than the interplanar distance) are possible — plastic flow. In a complex lattice of a ceramic consisting of several sublattices with its ion-covalent chemical-bond forces, cooperative motion is practically precluded, and only atom-wise transfer (diffusion) of ions differing by type, size, and charge with rigidly directed, strong bonds is possible. We note that diffusion mass transfer is also possible in metal crystals; it is especially noticeable at high temperatures (above $0.5T_{\text{melt}}$).

In practice we are ordinarily concerned with the behavior of comparatively large particles ($> 1 \mu\text{m}$), obtained by milling as well as by chemical methods but with much smaller sizes ($< 1 \mu\text{m}$). Actually, all powders have metastable particle states with high free energy. This is manifested in the high sorption capacity of gas and radicals as well as aggregation during the production process.

The existing data show [11] that powders with particle size of the order of 1 μm and larger can be obtained during milling. Ordinarily, further comminution essentially stops, and only some amorphization of the near-surface layers and disruption of the regularity of their lattice as a result of the formation of stress concentrators is observed. It is believed that energy accumulation in this case is achieved as a result of the appearance of new interfaces and lattice defects, i.e., energy is stored in the form of an excess energy of defects — vacancies, dislocations, block and crystal boundaries — as well as in the form of new surfaces, both internal and external. As a result of the increase of the internal energy, after reaching a certain state under the mechanical action of the milling bodies the highly disperse particles stop decreasing in size and the reverse process is observed — formation of quite strong conglomerates (aggregates) of particles and adhesion forces cause particles to stick to one another. This is a manifestation of the system striving to withstand the external action and decrease the level of internal energy, since aggregation is accompanied by partial compensation of the free chemical bonds of the surface atoms (ions). Another reason for the stopping of further comminution is the high strength of the small, practically defect-free, crystals.

We call attention to the main characteristic feature of the particles obtained by mechanical comminution: ordinarily they preserve the crystal structure, though it is possible for high degrees of lattice distortion to appear, right up to the formation of amorphized near-surface layers. A compact made from milled powders is far removed from a state of equilibrium because of the extended free surface and the presence of excess vacancies, stacking faults, dislocation, cracks, and so forth. Some authors believe that such powders are “active,” even though this concept remains undefined — a powder that sinters more rapidly and better at lower temperatures as compared with other powders is said to be active; it is believed that it is precisely defects and the mechanical stresses associated with them that are responsible for the activity.

Chemical methods are also used to introduce modifying additives, which change the sintering and the properties of a ceramic in the desired direction. The large departure from equilibrium promotes a uniform distribution of the additives, since there is not enough time for them to separate in the form of individual phases.

As practice shows, the highly disperse oxide powders obtained by modern chemical methods are very active to sintering. Ordinarily, the dispersity of such powders is less than 1 μm , i.e., it lies in the nanometer range. As a rule, powders consist of comparatively large aggregates, in which the small particles of the order of ten nanometers in size are bound to one another by adhesion forces. Aggregation is due to the overlapping of partially compensated bonds of surface atoms. The formation of a large number of surface defects — vacancies, dislocations — is characteristic for such particles.

When a solid particle arises under strongly nonequilibrium conditions, the overlapping of the chemical bonds of neighboring atoms occurs in a random, disordered manner, loosely, with formation of a large number of different kinds of structural imperfections. In addition, the distribution of the defects over the cross section of a particle is nonuniform: their concentration is higher at the surface. Consequently, it can be supposed that as the dispersity increases the role of the surface layer increases, since its fraction in the volume increases. It should be kept in mind that the surface of such particles is qualitatively different from the surface of large particles, since they consist of atoms with partially compensated chemical bonds and the sites surrounding them in the cell are not all occupied.

Thus, because the process of formation of a new phase is a highly nonequilibrium one, the powder particles have a rounded shape with a fractal surface structure and strongly distorted crystal structure — they are x-ray amorphous.

Another aspect of such a state is manifested in the appearance of strong hydrostatic forces in finely disperse particles because of the increase of the surface tension. Thus, for particles about 1 μm in size the compression forces are approximately 0.5 MPa and increase as the dispersity of the powder increases. The strong compressive forces of surface tension in nanoparticles are one reason for the instability of the state of the body; another reason is the high concentration of imperfections. They lead to losses of stability. For example, an appreciable decrease of the melting temperature of such powder as compared with a monolith is observed on heating.

Thus, it can be supposed that there are two ranges of powder particle sizes where particles accumulate energy by substantially different mechanisms. The boundary between these two ranges can be conventionally defined as lying between the micron and nanometer size ranges. Powders with particles larger than 1 μm accumulate energy in the form of the energy of free surfaces with zero curvature and in the form of the energy of defects in the crystal lattice. For powders with particles smaller than 1 μm an increase of the energy of atoms (ions) with uncompensated chemical bonds, located on surfaces, steps, ledges, and corners of nanosize particles. It is important that the state of such atoms is close to a surface state, so that the formation energy of the corresponding vacancies with respect to quasichemical reactions is close to the formation energy of surface vacancies.

We note that the mechanisms considered above by which a body accumulates energy actually represent a change of the state of the chemical bonds, specifically, distortion of the bonds under mechanical stresses, partial compensation of the with formation of new surfaces, ledges, and so forth, i.e., further distortion of the lattice up to amorphization with the transition to fine particles of the order of 10 nm in size. The formation of vacancies with the introduction of additives into the lattice also increases their internal energy as a result of the distortion of the bonds.

The x-ray diffraction patterns of the highly disperse powders do not, as a rule, carry any information about their crystalline structure. The powders are said to be x-ray amorphous. Since an x-ray photograph shows the pattern of the diffraction of x-rays by the crystal lattice, it can be concluded that in this case we have an amorphous state, for which only short-range order is characteristic and the bonds are spherically symmetric with no preferred directions. Therefore, particles with such sizes strive to take the shape of drop of liquid. In addition, amorphous particles must show viscous behavior, similarly to drops of liquid, and easily adjust to one another — they coalesce. The strong surface tension forces promote this.

The differences in the states of the two types of powders identified above determine their behavior during sintering. We shall examine the particularities of the mechanisms which intensify (activate) sintering processes, keeping in mind the model of viscodiffusive flow. The flow of an amorphous body can also be studied from this standpoint, provided that the body is represented as a strongly disordered crystal.

On the basis of the concepts expounded in [5], the origin of vacancies in crystals does not depend on the conditions — they are all equivalent. Consequently, we shall consider the diffusion coefficient D to be given by the product

$$D \sim n\mu,$$

where n is the concentration and μ is the mobility of the vacancies.

The mobility is structure-sensitive; it is determined by the easiest diffusion path and increases in the series volume — dislocation — boundary — surface (internal and then external). Thus, a vacancy follows the sites with weakened chemical bonds, and for solids the process proceeds with the expenditure of external energy.

The vacancy concentration is determined by the activation mechanisms, i.e., the formation of vacancies, which proceed as a result of the energy supplied to and accumulated by the body. The foregoing analysis shows that the most effective factor which makes it possible to vary the concentration over wide limits reversibly is thermal activation (i.e., heating), but only within a small range. All sources of accumulated energy (lattice deformation and lattice defects, surfaces with nonzero curvature, partially compensated chemical bonds) supply an appreciably larger number of vacancies, but they become exhausted and irreparable with time. A special case is the formation of vacancies and lattice deformation accompanying the introduction of foreign atoms: the excess energy of the partially realized chemical affinity maintains a constant and regulatable concentration of point defects.

Such a state of the particles affects their behavior during sintering under conditions of heating. One can imagine that as they grow the small “drops” which coalesce will exhibit the properties of crystals, i.e., definite growth directions and

planes will arise in them, which in the total force field will not differ sharply for individual particles — the field will orient them. Correspondingly, large neighboring particles likewise will not be strongly disoriented, which permits crystals to grow by adjustment without mass transfer over appreciable distances. The force field generated by the overall crystal lattice promotes this. It should be noted that such phenomena can be observed only in sufficiently pure crystals of compounds or solid solutions, since the segregation of impurities on the boundaries impedes adjustment.

Two different sintering mechanisms due to the presence of crystal lattice distortions can be imagined.

The first one consists of the viscodiffusive flow and is due to the flow of vacancies from source to sink in the force field due to surface tension in the presence of sections of the surface with nonzero curvature. The rate of the process is determined by the effective diffusion coefficient, which is determined by the concentration and mobility of the vacancies. Their form determines the concentration: thermal, impurity, and nonstoichiometric. In addition, irrespective of their origin in the crystal, all vacancies participate in mass transfer. The experimental data show that the number of carriers is most effectively regulated by introducing heterovalent impurities which enter the lattice as a solid solution [6]. The vacancy mobility is determined by the form of the path along which a vacancy emerges at the surface of the body, i.e., by the form of the lattice defect which facilitates its motion (dislocation, boundary, surface). Thus, the mobility carries the structure-sensitive part of the diffusion coefficient.

The second mechanism of sintering is characteristic mainly for highly disperse and highly defective powders obtained by chemical methods. The driving force is the same — surface tension, and the mechanism is the same — viscodiffusive flow. However, a mechanism of adjustment by means of shear, turning of atoms (ions) over a distance of the order of one unit cell (i.e., by simple restructuring of the bonds in the boundary layers of the cell) is added to it. The result is merging of neighboring crystals (particles). The high degree of defectiveness, when the state of the particles is closer to being amorphous than crystalline, promotes this. In addition, the atoms (ions) comprising a particle have an elevated energy, close to that of surface atoms. Actually, the body in this case comprises a viscofluid system of small particles and pores of nanometer size, and good adjustment is maintained up to large particle sizes, so that they manifest plasticity.

We call attention to a difference in the behavior of powders of this type.

Since the state of the particles in the two size ranges indicated above is qualitatively different, the diffusion mass transfer of the particles during sintering proceeds in part by different mechanisms. Large particles become harder and densify mainly by viscodiffusive flow; the sources and sinks of vacancies change at different stages and the diffusion path, which they traverse on the surfaces of the pores, boundaries, and volume of the crystals, is thereby limited by the coeffi-

cient of surface, boundary, and volume diffusion. However, at the early stage of the process, after the particles coalesce, the blank comprises a single highly porous medium, consisting of small pores and particles; it exhibits viscous flow under surface tension forces and deforms as a single body. This explains the high rate of shrinkage at the initial stages of sintering, before the onset of recrystallization, which pores impede.

In turn, recrystallization, proceeds in two stages — formation of centers of recrystallization and their growth up to the appearance of a continuous network of boundaries, after which crystals grow by the first mechanism. Since a blank consisting of comparatively large particles, greater than 1 μm in size, always contains small but distinct crystals, they are centers of crystallization, and the initial stage of recrystallization is practically absent. Sintering of large particles (i.e., conventional powders) proceeds in three stages. Here it should be noted that the final stage at which the pores do not impede the motion of the boundaries is accompanied by the growth of crystals, and as a rule by an increase of the sizes with virtually no decrease of the pore volume. This is observed when the total porosity reaches about 7%; in the best case the porosity decreases to 2–3% and the articles are characterized by inadequate strength, electrophysical, and other parameters.

During sintering, a blank made from highly disperse powder deforms practically as a defective matrix where the lattice defects are closer to the surface and chemical bonds are only partially compensated. A dense network of short boundaries between small particles does not permit crystal growth processes to develop, and pores are effective obstacles to the motion of boundaries as a single whole. The particles move conservatively by means of shear and turning during adjustment. The pores in the matrix do not close but rather “float upward” (as in a liquid) by diffusion. Crystals grow with low porosity and with pores smaller than a critical size (i.e., they overgrow). As a result, a nonporous and transparent state of the ceramic is reached. Apparently, nano-range powders exhibit special behavior, and here one must talk about not atoms on a surface but rather about the surface state of atoms or the surface state of the material. Such atoms have a low Fermi level. The state of highly disperse powders is inherited in fine-crystalline ceramic made using such powders, and the ceramic has a more open structure. This is manifested as a decrease of the hardness, index of refraction, and melting temperature of the ceramic.

Highly disperse blanks comprise a fine-crystalline, high-porosity medium with inclusions of small pores, which deforms rapidly. This is determined by the high curvature of the surface of the particles, which is inversely proportional to their radius. The surface of the particles is strongly extended and is under strong forces, determined by the product of the surface tension and the specific surface area. All this is a rea-

son for the formation of high local supersaturation of vacancies, which, in turn, have a high mobility along the surface. Most likely, the body must be regarded as a single whole. Therefore, to a first approximation, volume models of deformation can be used, though all vacancy characteristics must be surface characteristics (concentration, mobility). However, in this case, the qualitatively different state of the particles and the boundaries between them, which influence their behavior, is not adequately taken into account. Specifically, as the crystals grow their boundaries cannot detach from such small pores with a large curvature of the surface.

In summary, real powders, where large and small particles are present, will exhibit intermediate behavior. However, experience gained from studying refractories which contain large particles as well as a viscous medium (glass phase) shows something different. The mechanism of deformation of such a system is close to that of a rapidly deforming, fine-pore, highly disperse matrix. Large particles only increase the viscosity of the body effectively, i.e., the decrease the shrinkage rate somewhat.

REFERENCES

1. I. Ya. Guzman (ed.), *Chemical Technology of Ceramics and Refractories* [in Russian], OOO RIF “Stroimaterialy,” Moscow (2005).
2. *Soviet Encyclopedic Dictionary* [in Russian], Sov. Éntsikl., Moscow (1985).
3. V. A. Ivensen, *Phenomenology of Sintering* [in Russian], Metallurgiya, Moscow (1985).
4. O. N. Popov and P. T. Rybalkin, *Production and Application of Flux-Cast Refractories* [in Russian], Metallurgiya, Moscow (1985).
5. Ya. E. Geguzin, *The Physics of Sintering* [in Russian], Nauka, Moscow (1984).
6. Ya. I. Frenkel’, “Viscous state of solids under surface tension,” *Zh. Tekh. Fiz.*, **16**(1), 29–34 (1946).
7. B. Ya. Pines, “On solid-phase sintering,” *Zh. Tekh. Fiz.*, **16**(6), 737–745 (1946).
8. V. S. Bakunov and A. V. Belyakov, “Contribution to the analysis of the structure of a ceramic,” *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **32**(2), 243–248 (1996).
9. N. V. Solomin, “Investigation of the deformation of refractory materials under a load and the effective viscosity at temperatures up to 2800°C,” *Ogneupory*, No. 4, 183–188 (1950).
10. V. S. Bakunov and E. S. Lukin, “Particularities of the technology of high-density ceramic. Activity of active powders during sintering,” *Steklo Keram.*, No. 11, 21–25 (2008).
11. G. S. Khodakov, *The Physics of Comminution* [in Russian], Nauka, Moscow (1972).
12. Van Buren, *Defects in Crystals* [Russian translation], Inostr. Lit., Moscow (1962).
13. J. Friedel, *Dislocations*, Oxford (1964).
14. V. N. Chebotin, *The Physical Chemistry of Solids* [in Russian], Khimiya, Moscow (1982).
15. V. S. Bakunov, “High-temperature creep of refractory ceramic. Particularities of the process,” *Ogneupory*, No. 12, 4–7 (1994).